

Form PTO-1390US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE
(Rev. 5-93)

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY'S DOCKET NO. **H 4420 PCT/US**

U.S. APPLICATION NO. (if known sec. 17 CFR 1.5)

10/069849

INTERNATIONAL APPLICATION NO.
PCT/EP00/08175

INTERNATIONAL FILING DATE
August 22, 2000

PRIORITY DATE CLAIMED
August 31, 1999

TITLE OF INVENTION

METHOD FOR COLOURING HAIR

APPLICANT(S) FOR DO/EO/US

Mustafa Akram and Rolf-Werner Haubold

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). **EXECUTED**
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment
 ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:.

Version with Markings to Show Changes Made;
Information Disclosure Citation (Form PTO-1449) and References; and
International Search Report

"Express Mail" mailing label number **EL615775335US**

U.S. Application No. (If known see CFR 1.36) <div style="font-size: 2em; font-weight: bold; margin-left: 100px;">10/069849</div>		INTERNATIONAL APPLICATION NO. PCT/EP00/08175		ATTORNEY'S DOCKET NUMBER H 4420 PCT/US	
17. ■ The following fees are submitted: Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO..... \$890.00 International preliminary examination fee paid to USPTO (37CFR 1.482) \$710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37CFR 1.445(a)(2))..... \$740.00 Neither international preliminary examination fee (37CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$1,040.00 International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$100.00				<div style="display: flex; justify-content: space-between;"> CALCULATIONS PTO USE ONLY </div>	
ENTER APPROPRIATE BASIC FEE AMOUNT =				Order No. <u>02-0115</u> \$ 890	00
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).				\$	
Claims	Number filed	Number Extra	Rate		
Total Claims	23-20 =1	3	X 18.00	Order No. <u>02-0115.01</u> \$ 54	0
Independent Claims	2-3 =1	0	X 84.00	\$	00
Multiple dependent claims (s)(if applicable) 0			+ 280.00	\$	00
TOTAL OF ABOVE CALCULATIONS =				\$ 944	00
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$ 944	00
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37CFR 1.492(f)).....				\$	
TOTAL NATIONAL FEE =				\$	00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$ 944	
				Amount to be: refunded	\$-----
				charged	
<div style="display: flex; justify-content: space-between;"> <div style="width: 60%;"> <p>a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed.</p> <p>b. ■ Please charge my Deposit Account No. <u>01-1250</u> in the amount of \$ 944.00 to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. _____.</p> <p>c. ■ The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-1250</u>. A triplicate copy of this sheet is enclosed.</p> <p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</p> </div> <div style="width: 35%; text-align: right;"> <p>SEND ALL CORRESPONDENCE TO: Henkel Corporation, Law Dept. 2500 Renaissance Blvd., Ste. 200 Gulph Mills, PA 19406.....</p> </div> </div> <div style="margin-top: 20px; text-align: right;"> <p><i>Kimberly R. Hild</i> SIGNATURE</p> <p>Kimberly R. Hild NAME ATTORNEY FOR APPLICANT 39,224 REGISTRATION NUMBER</p> </div>					

PATENT
Docket No. H 4420 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Akram, et al.

International Application No. PCT/EP00/08175
International Filing Date: August 22, 2000

Serial No. To be assigned **Examiner:** To be assigned

Filed: To be assigned **Art Unit:** To be assigned

Title: METHOD FOR COLOURING HAIR

"Express Mail Post Office to Addressee" service mailing label number EL615775335US

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

In the Specification (Using the English Translation):

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following paragraph:

**Docket No. H4420 PCT/US
PCT/EP00/08175**

-- CROSS REFERENCE TO RELATED APPLICATIONS

This application is a national stage application under 35 U.S.C. § 371 of international application PCT/EP00/08175 filed on August 22, 2000, the international application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 199 41 450.5 filed on August 31, 1999.

On page 1, on a separate line after the above inserted paragraph and before line 1, please insert the following header:

-- BACKGROUND OF THE INVENTION -- .

On page 2, on a separate line between lines 24 and 25, please insert the following header:

--SUMMARY OF THE INVENTION--.

On page 2, on a separate line between lines 29 and 30, please insert the following header:

-- DETAILED DESCRIPTION OF THE INVENTION --.

On page 30, line 1, please delete the heading "CLAIMS" and insert therefor:

-- What is claimed is: --

On a separate page, after page 31, please insert the enclosed Abstract of the Disclosure.

In the Claims

Please cancel Claims 1 to 17, without prejudice.

Please add the following new claims:

18. (NEW) A process for coloring keratin fibers comprising:

(a) applying a pretreatment composition onto keratin fibers, wherein the pretreatment composition comprises at least one substantive dye; and

(b) applying to the keratin fibers a coloring composition comprising at least one synthetic dye or synthetic dye precursor or combinations thereof, after applying the pretreatment composition.

19. (NEW) The process of claim 18, wherein the pretreatment composition is applied to the keratin fibers by spraying.

20. (NEW) The process of claim 18 wherein the substantive dye of the pretreatment composition is selected from one or more nitrobenzene derivatives, basic substantive dyes or triphenylmethane derivatives, or combinations thereof.

21. (NEW) The process of claim 20 wherein the substantive dye is selected from 3-nitro-4-aminophenol, 4-(3'-hydroxypropylamino)-3-nitrophenol, 1,4-bis-(β -hydroxyethyl)-amino-2-nitrobenzene, 1-(β -hydroxyethylamino)-2-nitro-4-aminobenzene, 1-(β -hydroxyethylamino)-2-nitrobenzene, 4-(β -hydroxyethylamino)-3-nitrophenol, HC Blue 2, Basic Blue 99, Basic Red 76, Basic Brown 16 or Basic Brown 17, or combinations thereof.

22. (NEW) The process of claim 21 wherein the substantive dye is present in the pretreatment composition in an amount of 0.001 weight percent to 20 weight percent, based on the total weight of the pretreatment composition.

23. (NEW) The process of claim 22 wherein the substantive dye is present in the pretreatment composition in an amount of 0.005 weight percent to 5 weight percent, based on the total weight of the pretreatment composition.

24. (NEW) The process of claim 22 wherein the pretreatment composition further comprises at least one fiber-structure-improving agent.

25. (NEW) The process of claim 18 wherein the pretreatment composition further comprises at least one fiber-structure-improving agent.

26. (NEW) The process of claim 25 wherein the fiber-structure-improving agent is selected from panthenol, one or more physiologically compatible panthenol derivatives, one or more plant extracts or honey, or combinations thereof.

27. (NEW) The process of claim 25 wherein the fiber-structure-improving agent comprises panthenol.

28. (NEW) The process of claim 18 wherein the pretreatment composition is contacted with the keratin fibers for 1 to 30 minutes before applying the coloring composition.

29. (NEW) The process of claim 28 wherein the pretreatment composition is contacted with the keratin fibers for 1 to 10 minutes before applying the coloring composition.

30. The process of claim 18 wherein the pretreatment composition has a pH ranging from 3 to 9.

31. The process of claim 30 wherein the pretreatment composition has a pH ranging from 4 to 8.

32. The process of claim 18 wherein the synthetic dye or synthetic dye precursor of the coloring composition comprises at least one oxidative dye precursor.

33. (NEW) The process of claim 32 wherein the oxidative dye precursor comprises at least one primary intermediate selected from p-phenylenediamine, p-toluylenediamine, p-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol or 2,4,5,6-tetraaminopyrimidine, or combinations thereof.

34. (NEW) The process of claim 33 wherein the oxidative dye precursor further comprises at least one secondary intermediate selected from 2-chloro-6-methyl-3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, 2,6-di-(β -hydroxyethylamino)-toluene, 2-methyl resorcinol or 1-naphthol, or combinations thereof.

35. (NEW) The process of claim 32 wherein the oxidative dye precursor comprises at least one secondary intermediate selected from 2-chloro-6-methyl-3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, 2,6-di-(β -hydroxyethylamino)-toluene, 2-methyl resorcinol or 1-naphthol, or combinations thereof.

36. (NEW) The process of claim 32 wherein the oxidative dye precursor is oxidized with an oxidizing agent comprising hydrogen peroxide.

37. (NEW) The process of claim 32 wherein the oxidative dye precursor is oxidized with an oxidizing system comprising one or more enzymes.

38. (NEW) A process for coloring hair comprising applying to hair a pretreatment composition comprising at least one substantive dye, and subsequently applying a coloring composition to obtain a uniform color over the length of the hair.

39. (NEW) The process of claim 38 wherein the pretreatment composition is applied to the hair by spraying the pretreatment composition onto the hair.

40. (NEW) The process of claim 38 wherein the pretreatment composition is applied to only the end portion of the hair.

REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claims 18 to 40 will be pending after entry of the present amendment. Claims 1 to 17 are being canceled without prejudice.

Amendment

The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance 37 CFR §1.78 and to claim priority to those applications listed therein.

Attached hereto is a marked up version of the changes made to the specification entitled "Version With Markings To Show Changes Made."

New Claims 18 to 40 replace original Claims 1 to 17, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

Claim	Support in Specification
18	page 2, lines 25 to 29
19, 39	page 4, lines 10 to 13
20, 21	page 3, lines 17 to 26
22, 23	page 3, lines 27 to 30
24, 25, 26, 27	page 4, lines 28 to page 5, line 16
28, 29	page 13, lines 6 to 9
30, 31	page 13, lines 14 to 16
32	page 14, line 1
33	page 15, lines 2 to 6
34, 35	page 16, lines 24 to page 17, line 3
36, 37	page 20, line 29 to page 21, line 14

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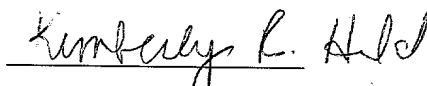
Claim	Support in Specification
38	page 22, lines 17 to 19
40	page 23, lines 3 to 7

No new matter is added by the new claims or amendments to the specification.

CONCLUSION

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,



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February 28, 2002

Henkel Corporation
Law Department
2500 Renaissance Boulevard, Suite 200
Gulph Mills, PA 19406

**Docket No. H4420 PCT/US
PCT/EP00/08175**

Abstract of the Disclosure

A method for coloring keratin fibers is provided that includes at least two steps. In one step, the keratin fibers are treated with a pretreatment composition containing at least one substantive dye. In another step, the keratin fibers are treated with a composition containing at least one synthetic dye or synthetic dye precursor after applying the pretreatment composition.

VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

On page 10, line 1, the heading "CLAIMS" has been amended as shown below:

[CLAIMS] What is claimed is:

Method for Coloring Hair

This invention relates to a two-stage process for coloring keratin fibers and to the use of a special pretreatment composition in this process.

Preparations for tinting and coloring hair are an important type of cosmetic product. They may be used to give the natural color of the hair a light or relatively dark shade, to obtain a totally different hair color or to cover unwanted color tones, for example gray tones, according to the wishes of the particular user. Conventional hair colorants are formulated either on the basis of oxidation dyes or on the basis of substantive dyes according to the required color or the permanence thereof. In many cases, combinations of oxidation dyes and substantive dyes are also used to obtain special shades.

Colorants based on oxidation dyes lead to brilliant and permanent color tones. However, they do involve the use of strong oxidizing agents, such as hydrogen peroxide solutions for example. Colorants such as these contain oxidation dye precursors, so-called primary intermediates and secondary intermediates. The primary intermediates form the actual dyes with one another or by coupling with one or more secondary intermediates under the influence of oxidizing agents or atmospheric oxygen.

Colorants based on substantive dyes do not require oxidizing agents and may be formulated at pH values near the neutral point. A major disadvantage of colorants based on substantive dyes is the poor fastness to washing of the colors obtained. In many cases, the capacity of the dye molecules for absorption onto the hair and the shine of the colored hair are not entirely satisfactory either.

Nevertheless, these known coloring methods are still not totally convincing. In many cases, an uneven color impression is created after coloring, particularly with the so-called fashionable shades in the red,

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copper and gold range, the hair fibers showing a loss of brilliance at their tips. This unevenness of coloring is attributable to the different care states of the hair fibers in the freshly regrown parts and the tips which may have become more porous through previous treatments or environmental influences. Accordingly, the problem addressed by the present invention was to provide a coloring process for keratin fibers which would not have the disadvantages mentioned above and which would lead to colors with excellent fastness properties.

It has now surprisingly been found that highly uniform colors with excellent fastness properties - even in the case of fashionable red, copper and gold shades - can be obtained if the fibers are treated in a first step with a pretreatment composition containing substantive dyes and are subjected in a second step to conventional coloring with at least one synthetic dye (precursor).

Two-stage processes for coloring keratin fibers have been known for some time. **WO 90/01922-A1**, for example, discloses a hair coloring process in which the hair is treated in a first step with a preparation containing a substantive dye and in a second step with a preparation containing natural dyes. However, there is nothing in that document which points to the advantages of the process according to the present invention. In many cases, such coloring processes were very complex and could only be carried out by professionals. In addition, the colors obtained with such processes were still not entirely satisfactory in regard to evenness and fastness.

In a first embodiment, therefore, the present invention relates to a two-stage process for coloring keratin fibers in which the fibers are treated in a first step with a pretreatment composition containing at least one substantive dye and in a second step with a conventional colorant containing at least one synthetic dye (precursor).

Keratin fibers in the context of the present invention are understood

to include pelts, wool, feathers and, in particular, human hair.

Substantive dyes are typically nitrophenylenediamines, nitroaminophenols, azo dyes, anthraquinones or indophenols. Preferred substantive dyes are the compounds known under the International names or commercial names of HC Yellow 2, HC Yellow 4, HC Yellow 5, HC Yellow 6, HC Yellow 12, Basic Yellow 57, Acid Yellow 1 (CI 10316), Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 2, Basic Red 76, Acid Red 87 (CI 45380), HC Blue 2, HC Blue 12, Disperse Blue 3, Basic Blue 7, Basic Blue 99, FD&C Green (CI 42053), D&C Green No. 8 (CI 59040), HC Violet 1, Basic Violet 14, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Acid Black 52, Basic Brown 16 and Basic Brown 17 and also 1,4-bis-(β -hydroxyethyl)-amino-2-nitrobenzene, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, hydroxyethyl-2-nitrotoluidine, picramic acid, sodium picramate, 2-amino-6-chloro-4-nitrophenol, 4-ethylamino-3-nitrobenzoic acid and 2-chloro-6-ethylamino-1-hydroxy-4-nitrobenzene.

Although the pretreatment composition may in principle contain any substantive dyes, nitrobenzene derivatives, basic substantive dyes and triphenyl methane derivatives have proved to be particularly suitable, particularly where coloring in the second stage is oxidative. Particularly preferred dyes for the purposes of the invention are 3-nitro-4-aminophenol, 4-(3'-hydroxypropylamino)-3-nitrophenol (HC Red BN), 1,4-bis-(β -hydroxyethyl)-amino-2-nitrobenzene, 1-(β -hydroxyethylamino)-2-nitro-4-aminobenzene (HC Red No. 3), 1-(β -hydroxyethylamino)-2-nitrobenzene (HC Yellow No. 2), 4-(β -hydroxyethylamino)-3-nitrophenol, HC Blue 2, Basic Blue 99, Basic Red 76, Basic Brown 16 and Basic Brown 17.

The pretreatment compositions according to the invention contain the substantive dyes in a quantity of preferably 0.001 to 20% by weight, more preferably 0.005 to 5% by weight and most preferably 0.01 to 1% by weight, based on the pretreatment composition as a whole.

The pretreatment composition according to the invention contains the substantive dyes in a suitable water-containing carrier. The pretreatment compositions may additionally contain other organic solvents such as, for example, methoxybutanol, benzyl alcohol, isopropyl alcohol, ethyl diglycol or 1,2-propylene glycol. Preferred solvents are any water-soluble organic solvents.

In addition, carriers according to the invention are creams, emulsions, gels or even surfactant-containing foaming solutions, for example shampoos, foam aerosols or other preparations suitable for application to the hair. Although there is nothing to prevent formulation of the pretreatment composition in any of the forms mentioned, it has proved to be of particular advantage in the interests of uniform coloring and easier handling to formulate the pretreatment composition as a spray.

In a particularly preferred embodiment, the pretreatment composition is formulated as a propellant-free pump spray. Nevertheless, it may also be formulated as a propellant-containing spray. In principle, any liquefiable gases used in the cosmetics field and air may be used as propellants. Such gases include, for example, lower alkanes, dimethylether and fluorochlorocarbons and fluorocarbons. The propellant(s) is/are preferably selected so that the preparations according to the invention form stable homogeneous mixtures even after prolonged periods under storage conditions typical of cosmetic products. Preferred propellants are lower alkanes, more particularly propane, butane, isobutane and mixtures of these alkanes.

The preparations according to the invention contain the propellants in quantities of preferably 1 to 20% by weight and more particularly 2 to 10% by weight, based on the preparation as a whole.

In a preferred embodiment of the present invention, the pretreatment composition contains a fiber-structure-improving agent besides the substantive dyes. Examples of such agents are panthenol and its

physiologically compatible derivatives. Such derivatives are in particular the esters and ethers of panthenol and cationically derivatized panthenols. Individual representatives are, for example, panthenol triacetate, panthenol monomethyl ether and its monoacetate and the cationic panthenol derivatives disclosed in **WO 92/13829**. Within this group, panthenol is particularly preferred.

Another suitable group of fiber-structure-improving agents are plant extracts.

These extracts are normally prepared by extraction of the whole plant. In some cases, however, it may even be preferable to prepare the extracts solely from blossoms and/or leaves of the plants.

So far as the plant extracts suitable for use in accordance with the invention are concerned, particular reference is made to the extracts listed in the Table beginning on page 44 of the **3rd Edition** of the **Leitfaden zur Inhaltsstoffdeklaration kosmetischer Mittel**, published by the **Industrieverband Körperpflege- und Waschmittel e.V. (IKW), Frankfurt**.

According to the invention, particular preference is attributed above all to the extracts of oak bark, stinging nettle, hamamelis, hops, camomile, burdock root, horse willow, hawthorn, lime blossom, almond, aloe vera, pine needle, horse chestnut, sandalwood, juniper, coconut, mango, apricot, lemon, wheat, kiwi, melon, orange, grapefruit, sage, rosemary, birch, mallow, lady's smock, creeping thyme, yarrow, thyme, balm, restharrow, coltsfoot, hibiscus, meristem, green tea ginseng and ginger root.

Particularly preferred extracts are those of oak bark, stinging nettle, hamamelis, hops, camomile, burdock root, horse willow, lime blossom, almond, aloe vera, coconut, mango, apricot, lemon, wheat, kiwi, melon, orange, grapefruit, sage, rosemary, birch, lady's smock, creeping thyme, yarrow, restharrow, meristem, green tea ginseng and ginger root.

The extracts of almond, aloe vera, coconut, mango, apricot, lemon, wheat, kiwi, melon and green tea are most particularly preferred for the use

according to the invention.

Water, alcohols and mixtures thereof may be used as extractants for preparing the plant extracts mentioned. Preferred alcohols are lower alcohols, such as ethanol and isopropanol, but especially polyhydric
5 alcohols, such as ethylene glycol and propylene glycol, both as sole extractant and in admixture with water. Plant extracts based on water/propylene glycol in a ratio of 1:10 to 10:1 have proved to be particularly suitable.

According to the invention, the plant extracts may be used both in
10 pure form and in dilute form. If they are used in dilute form, they normally contain ca. 2 to 80% by weight active substance and, as solvent, the extractant or extractant mixture used in their preparation.

In another preferred embodiment, mixtures of several, more particularly two, different plant extracts may be used in the compositions
15 according to the invention.

According to the invention, honey extracts are also preferred fiber-structure-improving agents. These extracts are obtained similarly to the plant extracts and normally contain 1 to 10% by weight and more particularly 3 to 5% by weight of active substance. Water/propylene glycol
20 mixtures can again be preferred extractants.

Other fiber-structure-improving agents are protein hydrolyzates, more particularly elastin, collagen, keratin, milk protein, soya protein, almond protein and wheat protein hydrolyzates, condensation products thereof with fatty acids and quaternized protein hydrolyzates. Fiber-
25 structure-improving agents also include mono-, di- and oligosaccharides such as, for example, glucose, galactose, fructose and lactose.

Certain amino acids may also be used as fiber-structure-improving agents for the purposes of the present invention. Examples are the amino acids serine, threonine and tyrosine described in **DE 195 22 569** to which
30 reference is specifically made here. Serine is a particularly preferred fiber-

structure-improving agent.

The pretreatment compositions according to the invention may also contain any of the known active substances, additives and auxiliaries typical of such preparations. In many cases, the pretreatment
5 compositions contain at least one surfactant, both anionic and zwitterionic, ampholytic, nonionic and cationic surfactants being suitable in principle. In many cases, however, it has been found to be of advantage to select the surfactants from anionic, zwitterionic or nonionic surfactants.

Suitable anionic surfactants for the hair colorants according to the
10 invention are any anionic surface-active substances suitable for use on the human body. Such substances are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group containing around 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether
15 and amide groups and hydroxyl groups may also be present in the molecule. The following are examples of suitable anionic surfactants - in the form of the sodium, potassium and ammonium salts and the mono-, di- and trialkanolammonium salts containing 2 or 3 carbon atoms in the alkanol group:

- 20 - linear fatty acids containing 10 to 22 carbon atoms (soaps),
- ether carboxylic acids corresponding to the formula $R-O-(CH_2-CH_2O)_x-CH_2-COOH$, in which R is a linear alkyl group containing 10 to 22 carbon atoms and $x = 0$ or 1 to 16,
- acyl sarcosides containing 10 to 18 carbon atoms in the acyl group,
- 25 - acyl taurides containing 10 to 18 carbon atoms in the acyl group,
- acyl isethionates containing 10 to 18 carbon atoms in the acyl group,
- sulfosuccinic acid mono- and dialkyl esters containing 8 to 18 carbon atoms in the alkyl group and sulfosuccinic acid monoalkyl polyoxyethyl esters containing 8 to 18 carbon atoms in the alkyl group and 1 to 6
30 oxyethyl groups,

- linear alkane sulfonates containing 12 to 18 carbon atoms,
- linear α -olefin sulfonates containing 12 to 18 carbon atoms,
- α -sulfofatty acid methyl esters of fatty acids containing 12 to 18 carbon atoms,
- 5 - alkyl sulfates and alkyl polyglycol ether sulfates corresponding to the formula $R-O(CH_2-CH_2O)_x-SO_3H$, in which R is a preferably linear alkyl group containing 10 to 18 carbon atoms and $x = 0$ or 1 to 12,
- mixtures of surface-active hydroxysulfonates according to **DE-A-37 25 030**,
- 10 - sulfated hydroxyalkyl polyethylene and/or hydroxyalkylene propylene glycol ethers according to **DE-A-37 23 354**,
- sulfonates of unsaturated fatty acids containing 12 to 24 carbon atoms and 1 to 6 double bonds according to **DE-A-39 26 344**,
- esters of tartaric acid and citric acid with alcohols in the form of addition
- 15 products of around 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols containing 8 to 22 carbon atoms.

Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids containing 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule and, in

20 particular, salts of saturated and, more particularly, unsaturated C_{8-22} carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

In the context of the invention, zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group

25 and at least one $-COO^{(-)}$ or $-SO_3^{(-)}$ group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example cocoacylaminopropyl dimethyl ammonium gly-

30 cinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing

8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name of Cocamidopropyl Betaine.

- 5 Ampholytic surfactants are surface-active compounds which, in addition to a C₈₋₁₈ alkyl or acyl group, contain at least one free amino group and at least one -COOH or -SO₃H group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkyl amidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkyl aminopropionic acids and alkyl aminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkyl aminopropionate, cocoacyl aminoethyl aminopropionate and C₁₂₋₁₈ acyl sarcosine.
- 10
- 15

Nonionic surfactants contain, for example, a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether groups as the hydrophilic group. Examples of such compounds are

- products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto linear fatty alcohols containing 8 to 22 carbon atoms, onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group,
- C₁₂₋₂₂ fatty acid monoesters and diesters of products of the addition of 1 to 30 moles of ethylene oxide onto glycerol,
- 20 - C₈₋₂₂ alkyl mono- and oligoglycosides and ethoxylated analogs thereof,
- products of the addition of 5 to 60 moles of ethylene oxide onto castor oil and hydrogenated castor oil,
- products of the addition of ethylene oxide onto sorbitan fatty acid esters,
- 25 - products of the addition of ethylene oxide onto fatty acid alkanolamides.

Examples of cationic surfactants suitable for use in the hair treatment compositions according to the invention are, in particular, quaternary ammonium compounds. Preferred quaternary ammonium compounds are ammonium halides, such as alkyl trimethyl ammonium chlorides, dialkyl dimethyl ammonium chlorides and trialkyl methyl ammonium chlorides, for example cetyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride and tricetyl methyl ammonium chloride. Other cationic surfactants suitable for use in accordance with the invention are the quaternized protein hydrolyzates.

Also suitable for use in accordance with the invention are cationic silicone oils such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning 929 Emulsion (containing a hydroxylamino-modified silicone which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, quaternium-80).

Alkyl amidoamines, particularly fatty acid amidoamines, such as the stearyl amidopropyl dimethyl amine obtainable as Tego Amid®S 18, are distinguished not only by their favorable conditioning effect, but also and in particular by their ready biodegradability.

Quaternary ester compounds, so-called "esterquats", such as the methyl hydroxyalkyl dialkoyloxyalkyl ammonium methosulfates marketed under the trade name of Stepantex® and the products marketed under the trade name of Dehyquart® - such as Dehyquart® AU-46 and Dehyquart® L-80 - are also readily biodegradable. The esterquats are the particularly preferred surfactants for the purposes of the invention.

One example of a quaternary sugar derivative suitable for use as a cationic surfactant is the commercially available product Glucquat®100 (CTFA name: Lauryl Methyl Gluceth-10 Hydroxypropyl Dimonium Chloride).

5 The compounds containing alkyl groups used as surfactants may be single compounds. In general, however, these compounds are produced from native vegetable or animal raw materials so that mixtures with different alkyl chain lengths dependent upon the particular raw material are obtained.

10 The surfactants representing addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of these addition products may be both products with a "normal" homolog distribution and products with a narrow homolog distribution. Products with a "normal" homolog distribution are mixtures of homologs which are obtained in the reaction of
15 fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. By contrast, narrow homolog distributions are obtained when, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. The use of products with
20 a narrow homolog distribution can be of advantage.

Other active substances, auxiliaries and additives are, for example,

- nonionic polymers such as, for example, vinyl pyrrolidone/vinyl acrylate copolymers, polyvinyl pyrrolidone and vinyl pyrrolidone/vinyl acetate copolymers and polysiloxanes,
- 25 - cationic polymers, such as quaternized cellulose ethers, polysiloxanes containing quaternary groups, dimethyl diallyl ammonium chloride polymers, acrylamide/dimethyl diallyl ammonium chloride copolymers, dimethyl aminoethyl methacrylate/vinyl pyrrolidone copolymers quaternized with diethyl sulfate, vinyl pyrrolidone/imidazolinium methochloride
30 copolymers and quaternized polyvinyl alcohol,

- zwitterionic and amphoteric polymers such as, for example, acrylamido-propyl/trimethyl ammonium chloride/acrylate copolymers and octyl acrylamide/methyl methacrylate/tert.butyl aminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers,
- 5 - anionic polymers such as, for example, polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert.butyl
- 10 acrylamide terpolymers,
- thickeners, such as agar agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, locust bean gum, linseed gums, dextrans, cellulose derivatives, for example methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, starch fractions and derivatives, such as
- 15 amylose, amylopectin and dextrans, clays such as, for example, bentonite or fully synthetic hydrocolloids such as, for example, polyvinyl alcohol,
- structurants, such as maleic acid and lactic acid,
- hair-conditioning compounds, such as phospholipids, for example
- 20 soybean lecithin, egg lecithin and kephalins, and also silicone oils,
- perfume oils, dimethyl isosorbide and cyclodextrins,
- cholesterol,
- light filters,
- consistency factors, such as sugar esters, polyol esters or polyol alkyl
- 25 ethers,
- fats and waxes, such as spermaceti, beeswax, montan wax, paraffins, fatty alcohols and fatty acid esters,
- fatty acid alkanolamides,
- complexing agents, such as EDTA, NTA and phosphonic acids,
- 30 - swelling and penetration agents, such as glycerol, propylene glycol

monoethyl ether, carbonates, hydrogen carbonates, guanidines, ureas and primary, secondary and tertiary phosphates,

- opacifiers, such as latex,
- pearlizers, such as ethylene glycol mono- and distearate,
- 5 - antioxidants.

There are no limits to the contact time of the pretreatment composition. However, it has proved to be of advantage for the contact time to be between 1 and 30 minutes, preferably between 1 and 10 minutes and most particularly between 3 and 5 minutes. Even though, in principle, there is no need for an intermediate treatment before conventional hair coloring in the second step, it has proved to be of advantage for excess liquid to be removed after the contact time by dabbing, stripping or drying before the second hair colorant is applied.

The hair treatment compositions according to the invention are preferably formulated so that they have a pH between 3 and 9, preferably between 4 and 8 and more preferably between 4 and 5. The pH may be adjusted with any of the acids and alkalizing agents used for this purpose in the cosmetics field.

The notion of conventional coloring with at least one synthetic dye (precursor) in the second step of the process according to the invention encompasses all processes known to the expert where a colorant is applied to the hair and is either left on the hair for a few minutes to ca. 45 minutes and then rinsed out with water or a surfactant-containing shampoo or is left entirely on the hair. Reference is specifically made in this connection to the known works which reproduce the relevant knowledge of the expert, for example Kh. Schrader, **Grundlagen und Rezepturen der Kosmetika, 2nd Edition, Hüthig Buch Verlag, Heidelberg, 1989.**

There are no basic restrictions to the composition of the conventional colorant.

Suitable dye (precursor)s include

- oxidation dye precursors of the primary and secondary intermediate type,
- synthetic substantive dyes and
- precursors of "nature-like" dyes, such as indole and indoline derivatives

and mixtures of representatives of one or more of these groups.

Oxidation dye precursors of the primary intermediate type are normally primary aromatic amines with another free or substituted hydroxy or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives and 2,4,5,6-tetraaminopyrimidine and derivatives thereof. Suitable primary intermediates are, for example, p-phenylenediamine, p-toluylenediamine, p-aminophenol, o-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenoxy)-ethanol, 4-amino-3-methylphenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2-dimethylamino-4,5,6-triaminopyrimidine, 2-hydroxymethylaminomethyl-4-aminophenol, bis-(4-aminophenyl)-amine, 4-amino-3-fluorophenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 4-amino-2-(diethylamino)-methyl-phenol, bis-(2-hydroxy-5-aminophenyl)-methane, 1,4-bis-(4-aminophenyl)-diazacycloheptane, 1,3-bis-(N-(2-hydroxyethyl)-N-(4-aminophenylamino))-2-propanol, 4-amino-2-(2-hydroxyethoxy)-phenol, 1,10-bis-(2,5-diaminophenyl)-1,4,7,10-tetraoxadecane and 4,5-diaminopyrazole derivatives according to **EP 0 740 931** or **WO 94/08970**, for example 4,5-diamino-1-(2'-hydroxyethyl)-pyrazole. Particularly advantageous primary intermediates are p-phenylenediamine, p-toluylenediamine, p-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine and 4-hydroxy-

2,5,6-triaminopyrimidine.

The primary intermediates p-phenylenediamine, p-toluylenediamine, p-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol and 2,4,5,6-tetraaminopyrimidine have proved to be particularly preferred, especially for obtaining fashionable colors.

m-Phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenol derivatives are generally used as oxidation dye precursors of the secondary intermediate type. Examples of such secondary intermediates are m-aminophenol and derivatives thereof such as, for example, 5-amino-2-methylphenol, 5-(3-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 2-hydroxy-4-aminophenoxyethanol, 2,6-dimethyl-3-aminophenol, 3-trifluoroacetyl-amino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-(2'-hydroxyethyl)-amino-2-methylphenol, 3-(diethylamino)-phenol, N-cyclopentyl-3-aminophenol, 1,3-dihydroxy-5-(methylamino)-benzene, 3-(ethylamino)-4-methylphenol and 2,4-dichloro-3-aminophenol,

- o-aminophenol and derivatives thereof,
- m-diaminobenzene and derivatives thereof such as, for example, 2,4-diaminophenoxyethanol, 1,3-bis-(2,4-diaminophenoxy)-propane, 1-methoxy-2-amino-4-(2'-hydroxyethylamino)-benzene, 1,3-bis-(2,4-diaminophenyl)-propane, 2,6-bis-(2-hydroxyethylamino)-1-methylbenzene and 1-amino-3-bis-(2'-hydroxyethyl)-aminobenzene,
- o-diaminobenzene and derivatives thereof such as, for example, 3,4-diaminobenzoic acid and 2,3-diamino-1-methylbenzene,
- di- and trihydroxybenzene derivatives such as, for example, resorcinol, resorcinol monomethyl ether, 2-methyl resorcinol, 5-methyl resorcinol, 2,5-dimethyl resorcinol, 2-chlororesorcinol, 4-chlororesorcinol, pyrogallol and 1,2,4-trihydroxybenzene,

- 5
- pyridine derivatives such as, for example, 2,6-dihydroxypyridine, 2-amino-3-hydroxypyridine, 2-amino-5-chloro-3-hydroxypyridine, 3-amino-2-methylamino-6-methoxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dihydroxy-4-methylpyridine, 2,6-diaminopyridine, 2,3-diamino-6-methoxypyridine and 3,5-diamino-2,6-dimethoxypyridine,
 - naphthalene derivatives such as, for example, 1-naphthol, 2-methyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-hydroxyethyl-1-naphthol, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,7-dihydroxynaphthalene and 2,3-dihydroxynaphthalene,
 - morpholine derivatives such as, for example, 6-hydroxybenzomorpholine and 6-aminobenzomorpholine,
 - quinoxaline derivatives such as, for example, 6-methyl-1,2,3,4-tetrahydroquinoxaline,
 - pyrazole derivatives such as, for example, 1-phenyl-3-methylpyrazol-5-one,
 - indole derivatives such as, for example, 4-hydroxyindole, 6-hydroxyindole and 7-hydroxyindole,
 - 20 - methylenedioxybenzene derivatives such as, for example, 1-hydroxy-3,4-methylenedioxybenzene, 1-amino-3,4-methylenedioxybenzene and 1-(2'-hydroxyethyl)-amino-3,4-methylenedioxybenzene.

25 Particularly suitable secondary intermediates are 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, resorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methyl resorcinol, 5-methyl resorcinol, 2,5-dimethyl resorcinol, 2,6-di-(β -hydroxyethylamino)-toluene and 2,6-dihydroxy-3,4-dimethylpyridine.

30 Most particularly preferred secondary intermediates, especially for

obtaining fashionable colors in the red range, are 2-chloro-6-methyl-3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, 2,6-di-(β -hydroxyethylamino)-toluene, 2-methyl resorcinol and 1-naphthol.

5 The primary/secondary intermediate combination of 2,4,5,6-tetraaminopyrimidine and 2-methyl resorcinol is particularly preferred for obtaining reddish shades.

So far as the substantive dyes suitable for the purposes of the invention are concerned, reference is made at this juncture to the foregoing observations.

10 Besides the synthetic dye (precursor), naturally occurring substantive dyes, such as, for example, henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, black alder bark, sage, logwood, madder root, catechu, sedre and alkanet, may also be used to obtain further shades.

15 Neither the oxidation dye precursors nor the substantive dyes have to be single compounds. On the contrary, other components may be present in small quantities in the hair colorants according to the invention due to the processes used to produce the individual dyes providing these other components do not adversely affect the coloring result or have to be
20 ruled out for other reasons, for example toxicological reasons.

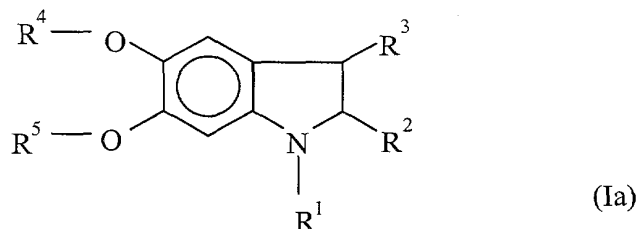
So far as the dyes suitable for use in the hair colorants and tinting compositions according to the invention are concerned, reference is also expressly made to the work by Ch. Zviak, **The Science of Hair Care, Chapter 7** (pages 248-250; substantive dyes) and **Chapter 8**, pages 264-
25 267; oxidation dye precursors), published as Volume 7 of the Series "Dermatology" (Ed.: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York/Basel, 1986, and to the **"Europäische Inventar der Kosmetik-Rohstoffe"** published by the Europäische Gemeinschaft and available on floppy disk from the Bundesverband Deutscher Industrie- und
30 Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel

d.V., Mannheim.

Both the oxidation dye precursors and the substantive dyes are present in the preparations according to the invention in quantities of preferably 0.01 to 20% by weight and more preferably 0.5 to 5% by weight, based on the preparation as a whole.

Preferred precursors of natural dyes are indoles and indolines which contain at least one hydroxy or amino group, preferably as a substituent on the six-membered ring. These groups may carry further substituents, for example in the form of an etherification or esterification of the hydroxy group or an alkylation of the amino group.

Particularly suitable precursors of natural hair dyes are derivatives of 5,6-dihydroxyindoline corresponding to formula (Ia):



in which - independently of one another - R^1 is hydrogen, a C_{1-4} alkyl group or a C_{1-4} hydroxyalkyl group,

R^2 is hydrogen or a $-COOH$ group, the $-COOH$ group optionally being present as a salt with a physiologically compatible cation,

R^3 is hydrogen or a C_{1-4} alkyl group,

R^4 is hydrogen, a C_{1-4} alkyl group or a group $-CO-R^6$, where R^6 is a C_{1-4} alkyl group, and

R^5 is one of the groups mentioned for R^4 ,

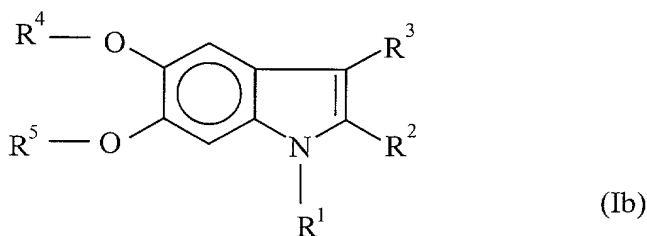
and physiologically compatible salts of these compounds with an organic or inorganic acid.

Particularly preferred derivatives of indoline are 5,6-dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-

propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline, 5,6-dihydroxyindoline-2-carboxylic acid and 6-hydroxyindoline, 6-aminoindoline and 4-aminoindoline.

Within this group, particular emphasis is placed on N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline and, in particular, 5,6-dihydroxyindoline.

Other particularly suitable precursors of natural hair dyes are derivatives of 5,6-dihydroxyindole corresponding to formula (Ib):



in which - independently of one another -

R¹ is hydrogen, a C₁₋₄ alkyl group or a C₁₋₄ hydroxyalkyl group,

R² is hydrogen or a -COOH group, the -COOH group optionally being present as a salt with a physiologically compatible cation,

R³ is hydrogen or a C₁₋₄ alkyl group,

R⁴ is hydrogen, a C₁₋₄ alkyl group or a group -CO-R⁶, where R⁶ is a C₁₋₄ alkyl group, and

R⁵ is one of the groups mentioned for R⁴,

and physiologically compatible salts of these compounds with an organic or inorganic acid.

Particularly preferred derivatives of indole are 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, 5,6-dihydroxyindole-2-carboxylic acid, 6-hydroxyindole, 6-aminoindole and 4-aminoindole.

Within this group, particular emphasis is placed on N-methyl-5,6-

dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole and, in particular, 5,6-dihydroxyindole.

The indoline and indole derivatives may be used both as free bases and in the form of their physiologically compatible salts with inorganic or organic acids, for example hydrochlorides, sulfates and hydrobromides, in the colorants used in the process according to the invention. The indole or indoline derivatives are present in these colorants in quantities of normally 0.05 to 10% by weight and preferably 0.2 to 5% by weight.

Where dye precursors of the indoline or indole type are used, it can be of advantage to use them together with at least one amino acid and/or at least one oligopeptide. Preferred amino acids are aminocarboxylic acids, more particularly α -aminocarboxylic acids and ω -aminocarboxylic acids. Among the α -aminocarboxylic acids, arginine, lysine, ornithine and histidine are particularly preferred. A most particularly preferred amino acid is arginine used more particularly in free form but also as the hydrochloride.

Hair colorants are normally adjusted to a mildly acidic to alkaline pH, i.e. to a pH of about 5 to 11, particularly where coloring is carried out oxidatively with atmospheric oxygen or other oxidizing agents, such as hydrogen peroxide. To this end, the colorants contain alkalizing agents, normally alkali metal or alkaline earth metal hydroxides, ammonia or organic amines. Preferred alkalizing agents are monoethanolamine, monoisopropanolamine, 2-amino-2-methylpropanol, 2-amino-2-methylpropane-1,3-diol, 2-amino-2-ethylpropane-1,3-diol, 2-amino-2-methylbutanol and triethanolamine and alkali metal and alkaline earth metal hydroxides. Within this group, monoethanolamine, triethanolamine and 2-amino-2-methylpropanol and 2-amino-2-methylpropane-1,3-diol are preferred. ω -Amino acids, such as ω -aminocaproic acid, may also be used as alkalizing agents.

If the actual hair colors are developed in an oxidative process, typical oxidizing agents such as, in particular, hydrogen peroxide or

adducts thereof with urea, melamine or sodium borate may be used. However, oxidation with atmospheric oxygen as sole oxidizing agent may be preferred. Oxidation may also be carried out with enzymes. In this case, the enzymes may be used both to produce oxidizing per compounds and to enhance the effect of an oxidizing agent present in small quantities.

Thus, the enzymes (enzyme class 1: oxidoreductases) are capable of transferring electrons from suitable primary intermediates (reducing agents) to atmospheric oxygen. Preferred enzymes are oxidases, such as tyrosinase and laccase, although glucoseoxidase, uricase or pyruvate oxidase may also be used. Mention is also made of the procedure whereby the effect of small quantities (for example 1% and less, based on the composition as a whole) of hydrogen peroxide is strengthened by peroxidases.

The preparation of the oxidizing agent is preferably mixed with the preparation of the oxidation dye precursors immediately before coloring of the hair. The ready-to-use hair coloring preparation formed should have a pH value in the range from 6 to 10. In a particularly preferred embodiment, the hair colorant is used in a mildly alkaline medium. The application temperatures may be in the range from 15 to 40°C but are preferably at the temperature of the scalp. After a contact time of about 5 to 45 and preferably 15 to 30 minutes, the hair colorant is removed from the hair to be colored by rinsing. There is no need for the hair to be washed with a shampoo where a carrier of high surfactant content, for example a coloring shampoo, has been used.

In the particular case of hair which is difficult to color, the preparation containing the oxidation dye precursors may be applied to the hair without preliminary mixing with the oxidation component. The oxidation component is applied after a contact time of 20 to 30 minutes, optionally after rinsing. After another contact time of 10 to 20 minutes, the hair is rinsed and, if desired, shampooed. In a first variant of this embodiment where the

preliminary application of the dye precursors is intended to improve penetration into the hair, the corresponding formulation is adjusted to a pH value of about 4 to 7. In a second variant, oxidation with air is initially carried out, the formulation applied preferably having a pH value of 7 to 10.

- 5 In the subsequent accelerated post-oxidation phase, it can be of advantage to use acidified peroxydisulfate solutions as the oxidizing agent.

Whichever of the processes mentioned above is used to apply the colorant according to the invention, development of the color may be supported and enhanced by adding certain metal ions to the colorant.

- 10 Examples of such metal ions are Zn^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Mn^{4+} , Li^{+} , Mg^{2+} , Ca^{2+} and Al^{3+} . Zn^{2+} , Cu^{2+} and Mn^{2+} are particularly suitable. Basically, the metal ions may be used in the form of a physiologically compatible salt. Preferred salts are the acetates, sulfates, halides, lactates and tartrates. Development of the hair color can be accelerated and the color tone can be influenced as required through the use of these metal salts.

The present invention also relates to the use of a pretreatment composition containing at least one substantive dye in a hair coloring process for obtaining a uniform color.

- 20 In one preferred embodiment of this use, the pretreatment composition is formulated as a spray. For further formulations, see the foregoing observations.

The following Examples are intended to illustrate the invention.

25

Examples

In the following Examples, all quantities are parts by weight unless otherwise stated.

Example 1

30

In a volunteer with dark blond hair with very porous tips, the hair was

divided by a center parting into a left-hand half and a right-hand half.

The left-hand half was treated as follows:

The porous hair tips were sprayed with ca. 15 g of formulation A1. After a contact time of 8 minutes at 25°C, the hair was treated over its entire length with a mixture of 30 g of formulation B1 and 30 g of a 6% aqueous hydrogen peroxide solution. After a contact time of 30 minutes at 25°C, the hair was rinsed with water, shampooed and blow-dried.

The right-hand half was treated as follows:

The hair was treated over its entire length with a mixture of 30 g of formulation B1 and 30 g of a 6% aqueous hydrogen peroxide solution. After a contact time of 30 minutes at 25°C, the hair was rinsed with water, shampooed and blow-dried.

Result:

The left-hand side was uniformly and intensively red in color from the roots to the tips. The right-hand side was less uniformly and less intensively red-colored.

Permanence test:

The hair was washed daily on both sides for 12 days with a commercially available shampoo. The result showed that color removal is greater on the right-hand side than on the left-hand side.

Formulation A1

	Natrosol® 250 HR ¹	0.2
	Dehyquart® L-80 ²	0.3
25	panthenol	0.1
	p-hydroxybenzoic acid methyl ester	0.03
	p-hydroxybenzoic acid propyl ester	0.03
	methoxybutanol	2.0
	4-hydroxypropylamino-3-nitrophenol	0.2
30	Basic Red 76	0.2

water

to 100

¹ hydroxyethyl cellulose (Hercules)

² bis(cocoyl)ethyl hydroxyethyl methyl ammonium methosulfate (INCI

5 name: Dicocoylethyl Hydroxyethylmonium Methosulfate, Propylene Glycol; Henkel)

Formulation B1

	ammonium carbopol solution, 1% in water ³	17.25
10	ammonium rohagit solution, 6% in water ⁴	5.25
	Oleth-7 ⁵	5.70
	potassium olein soap, 12.5% in water	3.45
	Plantaren® 2000 ⁶	0.53
	titanium dioxide anatase, type AS 05	0.48
15	Cetiol® V ⁷	3.45
	cetyl alcohol	16.80
	glycerol monostearate NSE ⁸	2.85
	phospholipid EFA ⁹	0.85
	tetrasodium EDTA	0.46
20	silica, highly disperse, pyrogenic	0.11
	p-toluylenediamine	0.1
	2,4,5,6-tetraaminopyrimidine	1.5
	2-methyl resorcinol	0.8
	2-amino-3-hydroxypyridine	0.05
25	HC Red BN	0.8
	HC Red 3	0.1
	methoxybutanol	1.43
	ammonia, 25% in water	to pH 10.0
	ascorbic acid	0.1
30	cetyl trimethyl ammonium bromide	0.5

perfume 0.43
water to 100

- 3 solution of an ammonium salt of a methacrylic acid/methacrylate
5 copolymer (INCI name: Ammonium Polyacrylate) (Röhm GmbH)
4 solution of an ammonium salt of an acrylic acid polymer (INCI name:
Ammonium Acrylates Copolymer) (Goodrich)
5 oleyl alcohol + 7 EO units (Henkel)
6 C₈₋₁₆-alkyl-1,4-polyglucoside (ca. 51% active substance; INCI name:
10 Decyl Glucoside) (Henkel)
7 oleic acid decyl ester (INCI name: Decyl Oleate) (Henkel)
8 (INCI name: Glyceryl Stearate) (Oleofina)
9 ca. 30% active substance; INCI name: Linoleamidopropyl PG
Dimonium Chloride Phosphate (Mona)

15

Example 2

In a volunteer with medium blond hair with very porous tips, the hair was divided by a center parting into a left-hand half and a right-hand half.

The left-hand half was treated as follows:

- 20 The porous tips were sprayed with ca. 10 g of formulation A2. After a contact time of 7 minutes at 25°C, the hair was treated over its entire length with a mixture of 30 g of formulation B2 and 30 g of a 6% aqueous hydrogen peroxide solution. After a contact time of 30 minutes at 25°C, the hair was rinsed with water, shampooed and blow-dried.

- 25 The right-hand half was treated as follows:

The hair was treated over its entire length with a mixture of 30 g of formulation B2 and 30 g of a 6% aqueous hydrogen peroxide solution. After a contact time of 30 minutes at 25°C, the hair was rinsed with water, shampooed and blow-dried.

- 30 Result:

The left-hand side was uniformly and intensively copper in color from the roots to the tips. The right-hand side was less uniformly and less intensively copper-colored.

Permanence test:

- 5 The hair was washed daily on both sides for 12 days with a commercially available shampoo. The result showed that color removal is greater on the right-hand side than on the left-hand side.

Formulation A2

10	Natrosol® 250 HR	0.2
	Dehyquart® L-80	0.3
	panthenol	0.1
	p-hydroxybenzoic acid methyl ester	0.03
	p-hydroxybenzoic acid propyl ester	0.03
15	methoxybutanol	2.0
	3-nitro-4-aminophenol	0.2
	water	to 100

Formulation B2

20	ammonium carbopol solution, 1% in water	17.25
	ammonium rohagit solution, 6% in water	5.25
	Oleth-7	5.70
	potassium olein soap, 12.5% in water	3.45
	Plantaren® 2000	0.53
25	titanium dioxide anatase, type AS 05	0.48
	Cetiol® V	3.45
	cetyl alcohol	16.80
	glycerol monostearate NSE	2.85
	phospholipid EFA	0.85
30	tetrasodium EDTA	0.46

	silica, highly disperse, pyrogenic	0.11
	p-toluylenediamine	0.4
	2-amino-3-hydroxypyridine	0.1
	3-methyl-4-aminophenol	0.3
5	resorcinol	0.06
	2-methylresorinol	0.04
	2-hydroxy-4-aminotoluene	0.2
	methoxybutanol	1.43
	ammonia, 25% in water	to pH 10.0
10	ascorbic acid	0.1
	cetyl trimethyl ammonium bromide	0.5
	perfume	0.43
	water	to 100

15 Example 3

In a volunteer with light blond hair with very porous tips, the hair was divided by a center parting into a left-hand half and a right-hand half.

The left-hand half was treated as follows:

20 The porous tips were sprayed with ca. 7 g of formulation A3. After a contact time of 5 minutes, the hair was treated over its entire length with a mixture of 30 g of formulation B3 and 30 g of a 6% aqueous hydrogen peroxide solution. After a contact time of 30 minutes at 25°C, the hair was rinsed with water, shampooed and blow-dried.

The right-hand half was treated as follows:

25 The hair was treated over its entire length with a mixture of 30 g of formulation B3 and 30 g of a 6% aqueous hydrogen peroxide solution. After a contact time of 30 minutes at 25°C, the hair was rinsed with water, shampooed and blow-dried.

Result:

30 The left-hand side was uniformly and intensively gold in color from

the roots to the tips. The right-hand side was less uniformly and less intensively gold-colored.

Permanence test:

The hair was washed daily on both sides for 12 days with a commercially available shampoo. The result showed that color removal is greater on the right-hand side than on the left-hand side.

Formulation A3

	Natrosol® 250 HR	0.2
10	Dehyquart® L-80	0.3
	panthenol	0.1
	p-hydroxybenzoic acid methyl ester	0.03
	p-hydroxybenzoic acid propyl ester	0.03
	methoxybutanol	2.0
15	HC Red 3	0.1
	HC Yellow No. 2	0.2
	water	to 100

Formulation B3

20	ammonium carbopol solution, 1% in water	17.25
	ammonium rohagit solution, 6% in water	5.25
	Oleth-7	5.70
	potassium olein soap, 12.5% in water	3.45
	Plantaren® 2000	0.53
25	titanium dioxide anatase, type AS 05	0.48
	Cetiol® V	3.45
	cetyl alcohol	16.80
	glycerol monostearate NSE	2.85
	phospholipid EFA	0.85
30	tetrasodium EDTA	0.46

	silica, highly disperse, pyrogenic	0.11
	p-toluylenediamine	0.5
	2-methylresorcinol	0.2
	resorcinol	0.05
5	2-amino-3-hydroxypyridine	0.05
	m-aminophenol	0.02
	4-chlororesorcinol	0.05
	methoxybutanol	1.43
	ammonia, 25% in water	to pH 10.0
10	ascorbic acid	0.1
	cetyl trimethyl ammonium bromide	0.5
	perfume	0.43
	water	to 100

CLAIMS

1. A process for coloring keratin fibers, characterized in that, in a first step, a pretreatment composition containing at least one substantive dye is applied to the fibers and, in a second step, the fibers are conventionally colored with at least one synthetic dye (precursor).
2. A process as claimed in claim 1, characterized in that the substantive dye of the pretreatment composition is selected from nitrobenzene derivatives, basic substantive dyes and triphenylmethane derivatives.
3. A process as claimed in claim 1 or 2, characterized in that the substantive dye is selected from 3-nitro-4-aminophenol, 4-(3'-hydroxypropylamino)-3-nitrophenol, 1,4-bis-(β -hydroxyethyl)-amino-2-nitrobenzene, 1-(β -hydroxyethylamino)-2-nitro-4-aminobenzene, 1-(β -hydroxyethylamino)-2-nitrobenzene, 4-(β -hydroxyethylamino)-3-nitrophenol, HC Blue 2, Basic Blue 99, Basic Red 76, Basic Brown 16 and Basic Brown 17.
4. A process as claimed in any of claims 1 to 3, characterized in that the pretreatment composition contains the substantive dyes in quantities of 0.001 to 20% by weight, preferably in quantities of 0.005 to 5% by weight and more particularly in quantities of 0.01 to 1% by weight, based on the pretreatment composition.
5. A process as claimed in any of claims 1 to 4, characterized in that the pretreatment composition is formulated as a spray.
6. A process as claimed in any of claims 1 to 5, characterized in that the pretreatment composition contains a fiber-structure-improving agent.
7. A process as claimed in claim 6, characterized in that the fiber-structure-improving agent is selected from the group consisting of panthenol, physiologically compatible panthenol derivatives, plant extracts and honey.
8. A process as claimed in claim 6 or 7, characterized in that the fiber-structure-improving agent is panthenol.

9. A process as claimed in any of claims 1 to 8, characterized in that the pretreatment composition is left on the hair for 1 to 30 minutes, preferably for 1 to 10 minutes and more particularly for 3 to 5 minutes.

10. A process as claimed in any of claims 1 to 9, characterized in that the pH of the pretreatment composition is in the range from 3 to 9, preferably in the range from 4 to 8 and more particularly in the range from 4 to 5.

11. A process as claimed in any of claims 1 to 10, characterized in that the conventional coloring step is an oxidative coloring step.

12. A process as claimed in claim 11, characterized in that a composition containing at least one primary intermediate selected from p-phenylenediamine, p-toluylenediamine, p-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol and 2,4,5,6-tetraaminopyrimidine as synthetic dye precursor is applied to the fibers in the second step.

13. A process as claimed in claim 11 or 12, characterized in that a composition containing at least one secondary intermediate selected from 2-chloro-6-methyl-3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, 2,6-di-(β -hydroxyethylamino)-toluene, 2-methyl resorcinol and 1-naphthol is applied to the fibers in the second step.

14. A process as claimed in any of claims 11 to 13, characterized in that the oxidative hair coloring step is carried out with hydrogen peroxide.

15. A process as claimed in any of claims 11 to 13, characterized in that the oxidative hair coloring step is enzyme-catalyzed.

16. The use of a pretreatment composition containing at least one substantive dye in a hair coloring process for obtaining a uniform color.

17. The use claimed in claim 16, characterized in that the pretreatment composition is formulated as a spray.

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☒ Declaration Submitted with Initial Filing OR ☐ Declaration Submitted after Initial Filing

Attorney Docket
Number

H 4420 PCT/US

First Named
Inventor

Akram, Mustafa

COMPLETE IF KNOWN

Application Number

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR COLOURING HAIR

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 08/22/2000 as United States Application Number or PCT International

Application Number PCT/EP00/08175 and was amended on (MM/DD/YYYY) _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority		Certified Copy Attached?	
			Not Claimed		YES	NO
199 41 450.5	Germany	08/31/1999	<input type="checkbox"/>		<input type="checkbox"/>	<input checked="" type="checkbox"/>
			<input type="checkbox"/>		<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>		<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>		<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>		<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>		<input type="checkbox"/>	<input type="checkbox"/>

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

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DECLARATION

Page 2

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112.1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/EP00/08175	08/22/2000	

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

<input type="checkbox"/> Firm Name		Customer Number	or label	
OR				

☒ List Attorney(s) and/or agent(s) name and registration number below:

Name	Registration Number	Name	Registration Number
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Kimberly R. Hild	39,224		
Steven C. Bauman	33,832		

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Please direct all correspondence to: ☒ Customer Number or label **00423** OR ☐ Fill in correspondence address below

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor:		<input type="checkbox"/> A petition has been filed for this unsigned inventor					
Given Name	Mustafa	Middle Initial		Family Name	Akram	Suffix e.g. Jr.	
Inventor's Signature	<i>Mustafa Akram</i>				Date	21.02.2002	
Residence: City	Hamburg	State		Country	Germany	Citizenship	Germany
Post Office Address	Zylinderbergstrasse 14						
Post Office Address							
City	22457 Hamburg	State		Zip		Country	Germany
Applicant Authority							

☒ Additional inventors are being named on supplemental sheet(s) attached hereto

(+) inside this box →

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DECLARATION				ADDITIONAL INVENTOR(S) Supplemental Sheet			
Name of Additional Joint Inventor, if any: <i>Rolf</i>				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
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City	22763 Hamburg	State		Zip		Country	Germany
Applicant Authority							
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
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City		State		Zip		Country	
Applicant Authority							
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
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City		State		Zip		Country	
Applicant Authority							
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
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City		State		Zip		Country	
Applicant Authority							
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
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